

## Digital conductometry for determination of boron in light water and heavy water at trace levels

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In-house built PC based rapid conductometric titration method for assay of trace amount of boron in light water and heavy water [100 ppb ( $\mu\text{g L}^{-1}$ )] with a precision of 2.2 has been reported. The method involves conversion of trace quantity of extremely poor conducting boric acid present in the sample to a relatively better conducting complexing species boron-mannitol complex using mannitol. This complex is then titrated against NaOH. Minor shift in conductivity during reaction of the complex compound with NaOH is captured online using an indigenously developed high resolution conductometric titration device. In addition, the technique provides information about any reactive chemical specimens, if present in the sample. The entire titration process is completed within a couple of minutes. A high resolution conductivity measurement technique has been proposed for quick assay of boron down to 20 ppb B level (RSD 4.1%). The present technique is suitable for rapid assay of boron in heavy water moderator in pressurised heavy water reactors. The influence of isotopic effect on sensitivity of measurements of boron in light water and heavy water matrices is also described.

**Keywords:** Boron – mannitol complex, Conductometric titration, Digital conductometry, Isotopic effect

Boron as boric acid and borate salts is used in many useful applications. Boric acid is generally used as a preservative in food and pharmaceutical industries<sup>1</sup>, whereas boron bearing compounds such as borate salts are mainly used in metallurgy, glass, fertilizer, electronics and cosmetic industries<sup>2-5</sup>. Such wide applications of boron compounds make the surrounding environment especially water source to be contaminated with boron. In water, boron is present in the form of boric acid and its concentration in drinking water lies between 300 ppb B and 1000 ppb B according to the World Health Organisation<sup>6</sup>. Hence, it is essential to monitor its concentration in drinking water. Another important use of boron is in nuclear power industries<sup>2,3,7</sup>. Controlled addition of boron in the form of boric acid to heavy water moderator is routinely adopted in pressurised heavy water reactors (PHWRs) as removable neutron poison material and its concentration is frequently monitored to ensure optimum reactor operation. Boron is commonly present as an impurity in nuclear fuel materials at sub-

ppm level. In order to monitor its chemical concentration in nuclear fuel, it is separated from the host matrix by steam distillation and analysed by using ion-chromatography<sup>8</sup>. Rao and Aggarwal<sup>9</sup> reported assay of boron in nuclear material such as uranium oxide using reversed phase HPLC.

Several analytical techniques, e.g. atomic absorption spectrophotometry (AAS)<sup>10</sup>, inductively coupled plasma atomic emission spectrometry (ICPAES)<sup>11,12</sup>, inductively coupled plasma mass spectrometry (ICPMS)<sup>13</sup>, neutron activation analysis<sup>14</sup>, HPLC<sup>8</sup>, flow injection analysis (FIA)<sup>15,16</sup>, sequential injection analysis with fluorimetric detector<sup>17</sup> and ion chromatography<sup>1</sup>, have been reported for assay of boron in aqueous solutions at trace levels. AAS is less sensitive and precise besides being susceptible to severe matrix interference. The HPLC method based on reverse – phase separation with diode array detector<sup>8</sup> and isotope dilution – thermal ionisation mass spectrometry (ID-TIMS)<sup>18</sup> for assay of boron in nuclear fuel materials at trace levels are highly sensitive techniques; but they are quite expensive. Similarly, ICPMS, ICPAES and neutron activation analysis provide excellent precision and sensitivity; but they are extremely expensive

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techniques. Such techniques have limited access to a few laboratories and they cannot be used for routine applications in industrial establishments. The FIA using a conductivity detector reported by Kumar *et al.*<sup>15</sup> is mainly recommended for the determination of boric acid in heavy water moderator samples. Though the authors have specified the range of analysis as 0 – 20 ppb, they have not worked out with light water or heavy water samples containing boron at ppb level which is required in nuclear power industry. Recently, ion chromatography is introduced in many nuclear power plants for assay of boron in heavy water moderator even down to 20 ppb B. Spectrophotometric techniques using either chromotropic acid originally developed by Kuemmel and Mellon<sup>19</sup> and further modified by Korenaga *et al.*<sup>20,21</sup> or chromogenic reagents such as curcumine and carminic acid<sup>22,23</sup> are recommended for the determination of boron at trace levels. The technique involves several chemical steps with excellent analytical skills and it is extremely time consuming process. These techniques are being followed by many skilled analysts to analyse many typical samples containing boron at trace levels in presence of several interfering specimens. However, for specific applications such as rapid and frequent analysis of boron in laboratories attached to nuclear power industries, such tedious techniques are not generally encouraged.

The brief review of analytical techniques reported for assay of boron shows that there is lack of simple, cost effective but highly precise and sensitive technique for rapid assay of boron in aqueous solution including heavy water matrix either present in relatively pure form or in association with some specific impurities. The ion chromatographic technique with conductivity detector, though highly convenient for quick assay of boron in water and heavy water needs specific training in operation and maintenance of the instrument. Furthermore, it needs frequent replacement of bed while used in routine analysis of samples in round the clock shifts. In order to address above problem, in this study a simple analytical technique based on conductometric approach has been proposed. This simple approach of addressing the problem was possible due to evolution of a high resolution, high precision and fast response conductivity monitoring device based on an unconventional approach of measurement of conductivity developed earlier<sup>24,25</sup>. In this work, a digital conductometric technique has been developed

and used for rapid assay of boron in light water and heavy water at trace levels, and the isotopic effect on sensitivity of measurement is demonstrated.

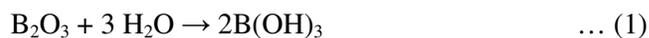
## Experimental Procedure

### Preparation of chemical reagents

All the chemical reagents used in this work were of analytical reagent (AR) grade. Millipore water having conductivity  $< 1.0 \mu\text{S cm}^{-1}$  (high purity de-ionised water abbreviated as DIW) was used for preparing all the reagents and standard solutions.

### Preparation of boric acid solution

When solid  $\text{B}_2\text{O}_3$  is dissolved in DIW, it forms boric acid according to the following reaction:



About 1.61 g of boron trioxide was dissolved in 500 mL DIW to produce a stock solution of  $1000 \mu\text{g L}^{-1}$  B. To 25 mL of aliquot about 2 g of mannitol was added and titrated against 1.0 M NaOH using phenolphthalein as indicator<sup>26</sup>. This stock solution was used to prepare dilute working standard solutions both at ppm ( $\text{mg L}^{-1}$ ) and ppb ( $\mu\text{g L}^{-1}$ ) levels with appropriate dilutions.

### Preparation of mannitol solution

About 20 g of mannitol (20% w/v) was dissolved in 100 mL of DIW. This was used in direct conductivity measurement approach recommended for the assay of boron. In conductometric titration, a fixed quantity of mannitol in solid form was added.

### Preparation of standard NaOH solutions

Sodium hydroxide (0.1M) solution was prepared as working standard solution and then standardized against oxalic acid. Further dilute solutions were freshly prepared directly from this working standard using appropriate dilution.

### Preparation of salt solutions

All salt solutions, such as NaCl, KCl, LiCl,  $\text{NaNO}_3$  and  $\text{Na}_2\text{SO}_4$ , used for interference study, were prepared by using respective salts. Appropriate concentrations of HCl and  $\text{NH}_4\text{OH}$  were prepared from respective analytical reagent grade chemicals and used for interference study.

### Heavy water

Heavy water with >99% isotopic purity, collected from Madras Atomic Power Station, Kalpakkam, India, was used in this work.

### Instrumentation

An indigenously made rapid titration device was used to carry out titrations both at ppm and ppb levels.

The detailed description of the titration device is described elsewhere<sup>27</sup> and this titration facility has been deployed in many critical applications at trace level analysis<sup>27,28</sup>. The conductivity sensor used in the present work consists of a pair of inert electrodes (platinum) which are placed in the sensing medium. This pair of electrodes constitutes a part of a specially designed miniaturized logic gate oscillator circuit (LGO) placed very close to the conductivity cell. If the cell is disconnected from the rest of the circuit it does not behave as LGO. When the oscillator is powered by very small power supply (5 V DC) it oscillates between 2 logic states, '0' or '1'. Hence, a train of rectangular pulses of 5V amplitude is generated from which frequency is determined. This frequency is related to the conductivity of solution. Since the primary signal obtained from the sensor is directly in digital domain form, without involvement of any analog to digital converter, pre-amplifier and post-amplifier, we name it as pulsating conductivity sensor and the approach of measurement of conductivity is known as digital conductometry.

#### Method

For measurement of boron in aqueous solution (in water or heavy water medium), using conductometric titration, an in-house built teflon cell of 50 mL capacity embedding a pair of platinum wires as electrodes and provision for flushing out dissolved carbon dioxide by argon purging was used. In some cases, a teflon beaker

was used for titration. A vertical type teflon probe with a pair of platinum electrodes was used to monitor the shift in conductivity during titration. The electrodes are part of an external oscillator circuit to produce digital pulses in proportion to conductance of liquid being sensed. A quick multipoint calibration method has been developed for conversion of frequency to conductivity. The relation between pulse frequency and conductivity in the range from  $< 1 \mu\text{S cm}^{-1}$  to  $50 \mu\text{S cm}^{-1}$  is expressed as:

$$\kappa = 2.9872e-7*f^2 + 3.822e-3*f + 0.19461 \quad \dots (2)$$

where  $\kappa$  is the specific conductance in  $\mu\text{S cm}^{-1}$ ; and  $f$ , the frequency in Hz.

A personal computer (PC) is used for pulse counting, data acquisition and processing. The entire titration process is carried out by using our laboratory developed software package in C- language.

A fixed volume of sample aliquot (25 mL or 50 mL) was taken in titration cell. About 0.5 g – 1 g mannitol was added to the sample. The solution was stirred to bring it into homogeneous solution. To this, standard NaOH (0.01 M or 0.005 M) was added in small volume steps (5 to 25  $\mu\text{L}$  step depending upon the sample concentration) using automated dispenser or by manual addition with Hamilton syringe for high precision work at trace level. The photograph of conductometric titration facility with a typical cell and an online titration plot of boric acid at ppm level is shown in Fig. 1. The detailed titration technique with



Fig. 1—Photograph of a laboratory made conductometric titration facility used for assay of boron at ppm and sub-ppm levels

online data acquisition in graphic form has been described elsewhere<sup>27,28</sup>. There is provision for titration of small volume (5 mL) of sample using a mini conductometric cell. Besides titration technique, direct conductivity measurement approach using our digital conductometry has also been used for quantitative assay of boric acid in the sample available in pure form. In this case, a series of standard boric acid solutions in pure water or heavy water matrix was prepared which covered an entire working range depending upon the application. To each standard solution, an appropriate volume of mannitol solution was added in order to bring overall concentration of mannitol in the sample matrix as 2 % (w/v). The shift in conductivity from blank solution, which was having similar conductivity as pure boric acid sample solution, was determined in each case. A calibration plot was prepared using shift in conductivity versus concentration of boron in ppm or in ppb depending upon the application. This polynomial relation was used in the system software in order to give direct reading of boron concentration in the real sample. This technique is recommended mainly for boric acid sample available in relatively pure form. However, in this study the proposed technique is also used for rapid assay of heavy water samples collected from the moderator system of a Pressurised Heavy Water Reactor.

## Results and Discussion

### Basic principle of technique

Boric acid is an extremely weak acid ( $pK_a = 8.98$ )<sup>1</sup> and as a result has insignificant effect on conductivity in aqueous solution. The conversion of extremely weak boric acid to boron-mannitol complex ( $pK_a = 4.1$ ) is well documented<sup>1,26</sup>. Boron-mannitol complex, though relatively stronger than pure boric acid, is also a weak acid. Hence, when boron is present at a few ppm or ppb levels it becomes extremely difficult to determine it either by direct conductometric measurement technique or by conductometric titration technique. The possibility of conductometric titration even at ppb B level was explored in this work with the help of high resolution conductometric titration device developed in-house. Moreover, it is also realized that when the medium of the matrix is changed from light water to heavy water the conductivity of solution further decreases even at a fixed concentration of boric acid. In short, in light water and heavy water matrices, boric acid-mannitol complex has been presented as HX and DX respectively, as shown below.



Hence, its extent of dissociation is purely concentration dependent. The nature of chemical reaction is same in heavy water matrix. Due to lesser mobility of  $D^+$  ion in heavy water compared to that of  $H^+$  ion in light water, conductivity changes are expected to be less in heavy water medium.

In the present work, two approaches are followed using a high precision as well as high resolution conductivity measurement technique to derive the quantitative information of boric acid in aqueous solution even at a few ppb B level. For a practically pure sample where it is possible to get a representative blank sample, the shift in conductivity before and after complexation with mannitol can be correlated directly to the boric acid concentration (approach-A). For situations where it is difficult to get blank sample of desirable purity a rapid conductometric acid base titration technique has been followed (approach-B). The break in titration plot at the stoichiometric end point is related to free boric acid complex and hence to boron content.

### Significant advancement in measurement capability

Using digital conductometry with pulsating sensor, it has been possible to monitor very minor shift in conductivity (down to  $20 \text{ nS cm}^{-1}$ ) in sample with excellent reproducibility in measurement. This, in turn, helps to get quantitative information of mannitol-complexed boric acid even at a few ppb B. This high resolution conductometric titration data as well as specific conductance measured in pure samples was possible due to the following distinguished features in sensing methodology:

(i) The sensing methodology permits practically noise free rapid response ( $< 100 \text{ ms}$ ) to ionic conductance sensed by a pair of platinum electrodes of appropriate geometry. Rapid response and high precision in measurement enable fast titrations with small volume of dilute solutions.

(ii) Sensor operation is entirely in digital domain starting from direct generation of a train of digital pulses from pulsating sensor compatible to PC. Unlike conventional sensors with analog signal this sensor does not require any signal conditioner.

(iii) Since the primary signal is directly in digital domain form, it can be easily transmitted over long distances to measuring devices.

(iv) The sensing electronics need very low power and driven by 5 V DC.

(v) The pulses are counted by PC under software control or in some cases by an external counter. The sensor is directly connected to PC through a signal routing unit without using any add-on card.

(vi) The software enables graphic display of signal in real time with respect to progress of reaction during titration, and quick data processing immediately after titration.

Due to these salient features of conductivity monitoring system we are able to deploy it in such a crucial application—trace level determination of boron.

#### Conductometric titration

The conductometric technique is basically non-specific. The overall conductivity is governed by the equivalent ionic conductances and concentrations of different species present in solution. This can be made specific by following the change in conductivity by reacting progressively one or more species with an external reactant. The slopes in the conductometric titration plots are characteristics of the species undergoing reaction. For determination of boric acid in aqueous solution the dissociated as well as undissociated fractions of the boric acid-mannitol complex are the species of interest for quantification.

Figures 2 and 3 show titration plots of boric acid complexed with mannitol versus standard NaOH in light water matrix at 100 ppb and in heavy water matrix at 200 ppb B respectively. In case of titration in DW matrix, 1 g mannitol is mixed with 50 mL DW containing 100 ppb B. The solution is flushed with Ar in order to remove dissolved carbon dioxide present in the sample solution. The sample has been titrated against 0.005 M NaOH in 10  $\mu$ L steps. The end point is 0.08 mL corresponding to 86 ppb B. In the same way, the titration has been conducted in heavy water matrix. The step of addition of titrant is 20  $\mu$ L, end point 0.18 mL corresponding to 194 ppb B. The conductivity titration plots in light water (Fig. 2) and heavy water (Fig. 3) are different since dissociation constant of DX is lower than that of HX. The initial decrease in conductivity due to first few drops of addition of NaOH (in light water medium) is due to dissociated fraction of boric acid mannitol complex. Highly conducting  $H^+$  ions are replaced by less conducting  $Na^+$  ions. Such phenomenon is not observed in titration carried out in heavy water medium. In this case, the dissociation of free  $D^+$  ion is practically negligible. The increase in conductivity in Fig. 3 and in region-II of Fig. 2 is due to major undissociated fraction of boric acid mannitol complex. The undissociated boric acid mannitol complex (HX or DX) reacts with NaOH as follows:

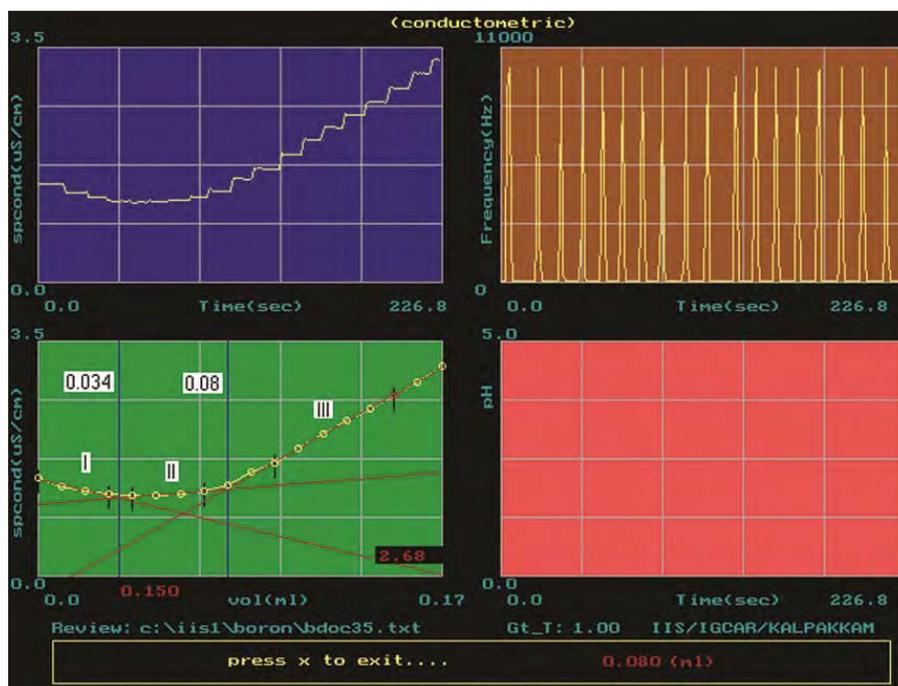


Fig. 2—Online titration plot of boric acid containing ~ 100 ppb B in light water medium

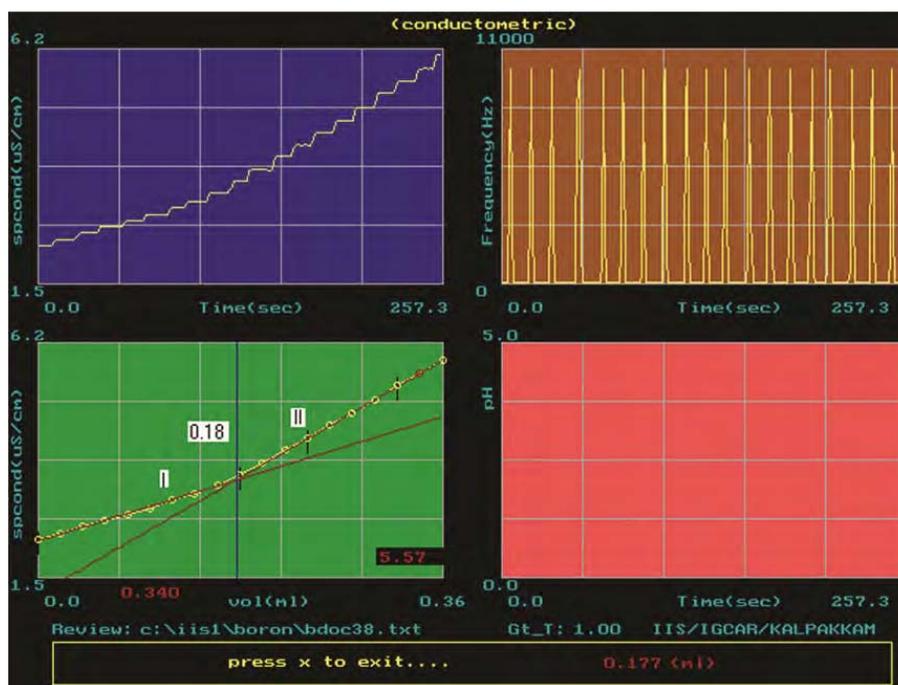
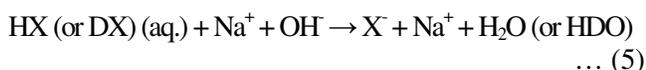


Fig. 3—Online titration plot of boric acid in heavy water matrix at sub-ppm level



Hence, weakly conducting HX (or DX) is replaced by  $\text{X}^-$  and  $\text{Na}^+$  ions with a positive slope, whereas after the end point the progressive increase in conductivity is due to accumulation of excess  $\text{Na}^+$  and  $\text{OH}^-$  ions. The equivalent ionic conductance of  $\text{OH}^-$  being significantly more than that of much larger and bulkier  $\text{X}^-$  ion, the slope of the post end point titration line is more than the pre end point titration line. The volume of  $\text{NaOH}$  consumed for stoichiometric reaction is derived from the point of intersection of these two lines differing in their slopes. This online titration plot is compared with a blank titration, plot containing no boron. In case of blank titration the conductivity gradually increases with step wise addition of standard  $\text{NaOH}$  solution. The precision in measurement for five independent titrations ( $n=5$ ) at 1 ppm B level is 0.015 ppm (RSD: 1.5%) and at 100 ppb B level is 2.2 ppb (RSD: 2.2%):

#### Influence of interfering salts

Non-interacting impurity will enhance conductivity of analyte solution to some extent which is purely dependent on its concentration. Hence, though the background conductivity will increase comparing to that of the pure system containing no impurity the contribution to overall conductivity shift remains

unchanged during titration. The decrease in conductivity due to replacement of  $\text{H}^+$  (dissociated part) with  $\text{Na}^+$  and increase in conductivity due to replacement of undissociated weakly conducting HX with more conducting  $\text{Na}^+$  and  $\text{X}^-$  appear in the titration plot like the pure system as shown in Fig. 2. Hence, the non-interacting impurities do not interfere in quantitative determination of boron. The 500 ppm of  $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{LiCl}$ ,  $\text{NaNO}_3$  and  $\text{Na}_2\text{SO}_4$  shows 1.0, 1.05, 0.96, 1.04 and 0.96 ppm boron respectively.  $\text{NaF}$  salt concentration of 200 ppm shows 1.05 ppm boron. It is observed that in some cases there is a difference of 4-5% in the results which can be minimized by reducing the step volume of reagent addition during titration.

#### Effect of reactive impurities

In presence of any acidic impurities, additional volume of  $\text{NaOH}$  will be consumed for neutralization and if the impurities are basic in nature less volume of  $\text{NaOH}$  is needed for the end point. Hence, the presence of such impurities gives erroneous results. Conductometric titrations were carried out with trace quantities of boron in presence of  $\text{HCl}$ ,  $\text{HF}$  and  $\text{NH}_4\text{OH}$ , and the observations are discussed hereunder.

The online titration plot in presence of known amount of  $\text{HCl}$  is given in Fig. 4. In this case about

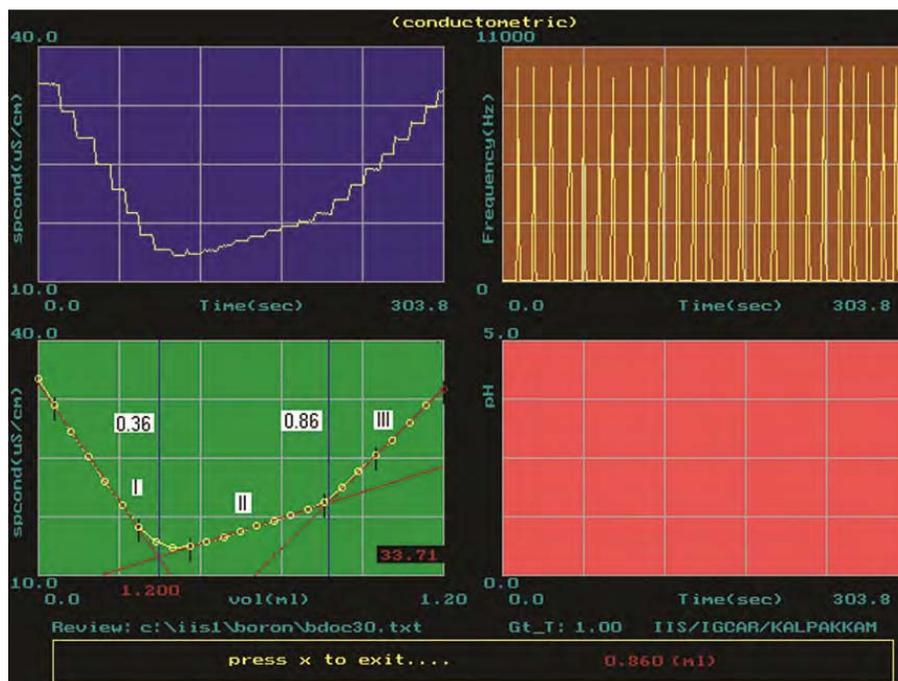
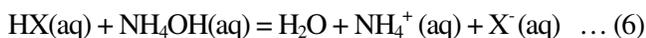


Fig. 4—Online titration plot of boric acid at 1 ppm B level in presence of trace quantity of HCl as impurity

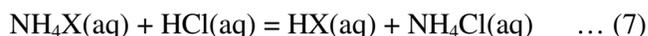
0.5 g mannitol has been added to 25 mL DW containing ~ 1 ppm B and 75  $\mu\text{M}$  HCl. The solution has been mixed well and titrated against 0.005 M NaOH in 50  $\mu\text{L}$  steps. Boric acid concentration in sample is 1.08 ppm B as against 1.0 ppm B. Initial steep decrease is due to the reaction of HCl with NaOH and, thereafter, the plot is similar to that of the boric acid complex. The first break corresponds to the HCl content. The difference in volumes between the second and the first breaks corresponds to the dissociated plus undissociated components of the boric acid mannitol complex. The result has been compared with another titration using boric acid of same concentration without adding HCl. The quantity of boric acid in both cases is found to be the same. Similar titration is also conducted by introducing HF to the boric acid-mannitol mixture.

In presence of basic impurities such as  $\text{NH}_4\text{OH}$ , a portion of the mannitol complexed boric acid, represented as HX, would react with  $\text{NH}_4\text{OH}$  as per the following reaction:



Hence, one will get lesser volume at end point than the expected value. In order to circumvent this difficulty, the starting solution is acidified with HCl before subjecting it to conductometric titration. It is found that the portion of HX, lost due to reaction with

$\text{NH}_4\text{OH}$ , reappears on account of the following reaction:



Conductometric titration against NaOH is found to be similar to what has been obtained earlier with HCl alone, permitting assay of boron quantitatively. In nuclear fuel sample B is present as trace impurity. By pyrohydrolytic distillation, it is separated from the sample matrix. In this separation process, trace impurities such as F, Cl and N are likely to be associated with condensates collected during pyrohydrolytic distillation. Hence, the present technique can be applied for assay of boron in nuclear fuel materials by slightly modifying the instrumentation parameter. Further work is in progress in this direction.

#### Assay of boric acid in potable water

Water samples collected from laboratory tap were filtered using Whatman-540 filter paper to remove suspended particles. Boric acid present in those samples was analysed using the present technique. An aliquot of water sample was passed through a strong cation exchange resin column in order to remove all cations present in the sample matrix. The pH of sample after passing through cation exchange resin bed is found to be between 2.8 and 3.2 due to conversion of

salts to their respective mineral acids, which is popularly known as equivalent free mineral acids (EMA), an important parameter in water chemistry. The sample was further titrated against standard NaOH using present technique. Boric acid concentration in laboratory tap water was about 0.5 ppm B. We also followed a standard addition technique to verify the result. To different aliquots of water sample containing boric acid of 0.5 ppm B, standard boric acid was added in order to bring the overall concentration between 1 ppm and 5 ppm B. After passing each sample aliquot through cation exchange resin column titration was conducted. The results obtained from titrations agree well with the predicted value. The online titration plot for boric acid present in tap water matrix is found to be similar to that obtained in titration of boron mannitol complex in presence of HCl as impurity. Results of filtered tap water sample aliquots with and without addition of excess boric acid are shown in Table 1. These results are also compared with those obtained from an independent spectrophotometric technique<sup>29</sup>. The % relative standard deviation (RSD) in the present technique lies between 1.6 and 2.7 as against 2.46 and 4.8 in spectrophotometric technique. The slightly higher RSD values in the spectrophotometric technique are accounted due to involvement of several chemical steps used before the measurement of absorbance. From the results (Table 1), it is observed that in some cases consistency in the precision with respect to concentration is not strictly maintained as expected theoretically. The present technique is a volumetric titration technique using high resolution conductometric titration device. The step addition of reactant in this case is 20 microlitre. With uncertainty in one drop in the end point the uncertainty in boron concentration varies from 0.08 ppm to 0.17 ppm. The precision as shown in each case in terms of drop volume is much less. Hence, in this case it is difficult to correlate precision with respect to change in analyte concentration. By reducing the step volume to 2 microlitre the correlation with respect to concentration may match. But it will take longer time for completion of titration. Without passing water sample through cation exchanger it can be titrated adjusting pH to ~3.5 using HCl to convert all carbonate and bicarbonate salts in water to H<sub>2</sub>CO<sub>3</sub> and removing it by flushing with argon for about 5 min before titration. We deliberately passed through cation exchanger in order to demonstrate separation of EMA and boron in the form of boron mannitol complex in a single titration.

#### Response of conductometric technique

Further experiments were conducted by using a high sensitive conductivity monitoring system to examine the response of shift in frequency due to minor increase in conductivity during complexation of trace boric acid with mannitol in light water and heavy water matrices. All measurements were conducted in inert atmosphere in order to avoid the contamination of atmospheric carbon dioxide. Table 2 shows stepwise increase in pulse frequency during addition of boric acid with rise in boron concentration

Table 1—Comparison of present titrimetric technique with spectrophotometric technique using tap water samples

Sample	Boron concentration (added), ppm	Boron concentration (found), ppm	
		Present titration technique	Spectrophotometry Curcumin method
S-1	Nil	0.5 ± 0.01 (RSD 2.0%)	0.46 ± 0.02 (RSD 4.3%)
S-2	0.5	1.1 ± 0.02 (RSD 1.8%)	0.93 ± 0.045 (RSD 4.8%)
S-3	1.0	1.46 ± 0.04 (RSD 2.7%)	1.5 ± 0.06 (RSD 4.0%)
S-4	2.5	3.11 ± 0.05 (RSD 1.6%)	3.25 ± 0.08 (RSD 2.46%)
S-5	4.5	5.0 ± 0.13 (RSD 2.6%)	4.9 ± 0.16 (RSD 3.2%)

Three aliquots of each sample were taken for both titration and for spectrophotometric analysis ( $n = 3$ ).

Table 2—Shift in pulse frequency in heavy water – mannitol and light water – mannitol mixtures with step-wise addition of boric acid at ppb levels

Sample	Concentration of boron, ppb	Measured frequency, Hz	Frequency shift from blank, Hz
Heavy water + mannitol (45 mL+5 mL 20% w/v)	0	6158.9 ± 0.6	0
	20	6177.8 ± 0.53	18.9
	40	6201.5 ± 0.51	42.6
	60	6228.9 ± 0.49	70
	79.9	6258.7 ± 0.44	99.8
	99.9	6289.8 ± 0.47	130.9
	119.9	6322.1 ± 0.35	163.2
	139.8	6356.1 ± 0.33	197.2
	159.7	6390.3 ± 0.47	231.4
	179.7	6425.5 ± 0.51	266.6
199.6	6461.3 ± 0.46	302.4	
Light water + mannitol (45 mL+5 mL 20% w/v)	0	3608.9 ± 0.37	0
	10	3665.2 ± 0.91	56.3
	20.0	3717.7 ± 0.73	108.8
	29.9	3767.3 ± 0.88	158.4
	39.8	3815.7 ± 1.0	206.8
	49.8	3862.7 ± 0.98	253.8

In each case, standard deviation is determined from 15 data points collected at 2s counting interval during measurement ( $n = 15$ ).

by about 10 ppb in case of light water and 20 ppb in case of heavy water respectively. The shift in pulse frequency from blank sample and concentration of boron in heavy water as mentioned in Table 2 shows the following polynomial relationship:

$$\begin{aligned} \text{R-square (COD)} &= 0.99907 \\ y &= -5.43979e-4*x^2 + 0.805*x + 4.02211 \quad \dots (8) \end{aligned}$$

Where  $y$  is the concentration of boron as ppb B; and  $x$ , the shift in pulse frequency from the blank. Using this relation, a typical heavy water sample containing about 20 ppb boron is determined. The precision in measurement is 0.82 ( $n=10$ ), RSD 4.1%.

It is observed that the frequency shift at every step is considerably less in heavy water than that in light water. It is due to the considerable decrease in ionic mobility of heavier isotope  $D^+$  ion comparing to that of lighter isotope  $H^+$  ion. Remarkably, high precision and high resolution in conductivity measurement enables capturing of small shift in specific conductance due to presence of boric acid mannitol complex at trace level in heavy water. The change in boron concentration by 10 ppb from blank level brought a change in frequency shift by 18 Hz in case of heavy water medium as against ~109 Hz in light water medium which is accounted due to isotopic effect as discussed above.

#### Validation of technique

The present conductometric techniques such as titrimetric and direct conductivity measurement are validated for the assay of boron in heavy water samples by comparing the results with those obtained from spectrophotometric technique and in some cases with ion chromatography. We used two types of samples, namely synthetic samples and two batches of heavy water samples containing boron from moderator system of a PHWR during normal reactor operation time and during start up of the reactor. The concentration of boron in a series of synthetic samples was determined by using conductometric titration as well as direct conductometric technique described in this paper. The relationship between shift in specific conductance and concentration of boron in heavy water upto 10 ppm B level, using direct conductometry, is expressed as:

$$y = 1.24518*x^2 + 1.10804*x - 0.05862 \quad \dots (9)$$

where  $y$  is the concentration of boron as ppm B; and  $x$ , the shift in conductivity ( $\mu\text{S cm}^{-1}$ ) from blank heavy water.

The concentration of boron in heavy water samples were determined by using the relation between shift in conductivity of sample from respective blank sample and concentration of boron as ppm B using the above calibration plot. Heavy water with conductivity very close to that of sample solution was used as a representative blank sample. A fixed volume of mannitol was added to blank sample in order to bring mannitol concentration to 2%(w/v). Finally, the conductivity of blank solution was measured after mannitol addition, let it be ' $\kappa_1$ '. The sample was treated in similar way and the conductivity was measured, let it be ' $\kappa_2$ '. The shift in conductivity of sample from blank i.e. ( $\kappa_2 - \kappa_1$ ) was determined. Using the calibration plot (shift in conductivity versus B concentration) the concentration of sample was determined. Results obtained by using both independent measurement approaches agree well (Table 3) which is further verified by spectrophotometric technique<sup>29</sup>.

The concentration of boron in each heavy water sample collected during normal reactor operation was measured by using the present technique (direct conductometric measurement approach) and ion chromatography, whereas the concentration of boron in heavy water samples collected during reactor start up time was determined by conductometric titration technique and spectrophotometry. The results are shown in Table 4. In ion chromatography Ion-pac IC

Table 3—Comparison of present techniques with spectrophotometric technique for the determination of boric acid in heavy water samples

Sample	Boron sought <sup>a</sup> [B], ppm	Boron found <sup>b</sup> [B], ppm		
		Present techniques		Curcumin spectrophotometric method
		Approach-B <sup>c</sup>	Approach-A <sup>d</sup>	
Sample-1	2.0	1.85 ± 0.03	1.9 ± 0.03	1.8 ± 0.06
Sample-2	1.5	1.51 ± 0.03	1.46 ± 0.03	1.48 ± 0.05
Sample-3	1.0	1.0 ± 0.01	0.92 ± 0.01	0.91 ± 0.035
Sample-4	2.5	2.45 ± 0.05	2.5 ± 0.05	2.42 ± 0.06
Sample-5	1.5	1.47 ± 0.02	1.52 ± 0.03	1.55 ± 0.05
Sample-6	0.5	0.48 ± 0.01	0.48 ± 0.01	0.51 ± 0.02
Sample-7	2.2	2.3 ± 0.04	2.32 ± 0.04	2.28 ± 0.06
Sample-8	1.6	1.57 ± 0.03	1.6 ± 0.03	1.54 ± 0.04

<sup>a</sup> Standard boric acid solution was prepared in heavy water matrix. Each synthetic sample was prepared by spiking appropriate aliquot of standard to a fixed volume of heavy water.

<sup>b</sup> Three aliquots of each sample were taken for analysis using above technique ( $n = 3$ ,  $n$  represents number of independent measurements).

<sup>c</sup> Approach-B Conductometric titration technique.

<sup>d</sup> Approach-A Direct conductivity measurement approach.

Table 4—Assay of boron in heavy water samples collected from the moderator system of a PHWR

Sample identification number	Concentration of boron			
	Present technique		Spectrophotometric (in ppm)	Ion chromatography (in ppb)
	App-A (in ppb)	App-B (in ppm)		
MAP-OP-1	20.1 ± 0.6	-	-	18.8 ± 0.7
MAP-OP-1	20.0 ± 0.64	-	-	19.9 ± 0.7
MAP-OP-1	19.8 ± 0.62	-	-	20.3 ± 0.64
MAP-OP-1	21.7 ± 0.58	-	-	20.8 ± 0.7
MAP-OP-1	24.5 ± 0.66	-	-	25.0 ± 0.7
MAP-OP-1	24.3 ± 0.61	-	-	25.1 ± 0.73
MAP-ST-1	-	1.03 ± 0.02	1.06 ± 0.03	-
MAP-ST-1	-	0.78 ± 0.01	0.65 ± 0.015	-
MAP-ST-1	-	1.2 ± 0.025	1.2 ± 0.02	-
MAP-ST-1	-	0.55 ± 0.01	0.51 ± 0.014	-
MAP-ST-1	-	0.55 ± 0.01	0.54 ± 0.015	-

MAP-O—Heavy water samples collected during normal operation period of the reactor,

MAP-ST—Heavy water samples collected during start-up of the reactor.

The uncertainty in measurement is determined in three aliquots of each sample ( $n = 3$  in each case).

borate column (9 x 250 mm) was used as the separation column. The optimum conditions for analysis are found to be (i) eluent 2.5 mM methane sulphonic acid (MSA) + 60 mM mannitol (ii) no concentrator nor suppressor (iii) loop volume 100 micro litre (iv) sample used in each analysis ~ 2.5 mL and (v) flow rate 1 mL min.<sup>-1</sup>, regenerant TMA hydroxide. Results obtained from the present technique and other conventional techniques agree well. Hence, the digital conductometric technique reported in this work is a simple approach for quick determination of boron in heavy water samples which seems to be attractive and more user friendly for the analysis of boron in heavy water moderator system of PHWR.

### Conclusion

A simple, accurate and highly reproducible analytical technique using a new type of conductivity monitoring instrument with conductometric titration facility has been presented for trace level determination of boron in aqueous solution. The titration with display of online titration plot and quick processing of data to get quantitative information of boron content in sample has been completed within a couple of minutes. The most interesting aspect of this titration technique is that one can get quantitative information of any reactive trace impurities present in the sample along with the desired specimen as a separate chemical specimen in the titration plot. Hence, for quantitative information on different

chemical species present in a composite sample, this digital conductometric titration technique is the simplest approach. Probably, this is the only titration technique for the assay of boron in water samples at sub-ppm levels. The present technique has been successfully examined for the determination of boron in water including potable drinking water and heavy water samples at ppm and ppb levels. In addition to this, high resolution titrimetric technique, direct conductivity monitoring approach with a high resolution conductivity meter has been proposed for rapid assay of boron in heavy water down to a few ppb levels in the context of rapid assay of boron in heavy water moderator system of PHWRs.

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